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Device and method for evaporation of a coating material

1. Technical field

The present invention relates to a device and a method for evaporating a coating material in vacuum ambient, particularly for the fabrication of coatings comprising complex inorganic compounds like high temperature superconductors.

2. State of the art

Thin films of complex inorganic compounds, e.g. oxides, nitrides, carbides or alloys of various cations, serve as functional coatings or surface hardening in many applications in electronics, optics and mechanical engineering. For example films of PZT (Lead-zirconium-titanate) ceramics or BaTiO_3 are used for ferroelectric sensor elements or data memories with high dielectric constant. Thin epitaxial layers of $\text{RBa}_2\text{Cu}_3\text{O}_7$ (R = yttrium or a rare earth element) become superconducting at low temperatures and can be used e.g. in communication technology for highly selective radio frequency filters, or deposited on flexible metal tapes for conducting electrical current without losses.

For the economic use for many of these applications large areas or long lengths (coated conductors) have to be coated in the possibly shortest time. Since many compounds only exhibit the desired properties if the film is of high crystalline perfection, the requirements on the coating technology are very demanding. Further, for mixed compounds the correct stoichiometric composition has to be guaranteed across the entire deposition area and for the whole duration of the coating process.

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As a rule, the deposition is performed by vacuum coating techniques like sputtering, Laser ablation (PLD), chemical vapor deposition (CVD), molecular beam epitaxy (MBE), or evaporation. For those techniques that start from non-conductive, ceramic compounds (targets) (e.g. sputtering, PLD) the volume deposition rate is usually very low. Techniques like CVD or co-evaporation, as described for example in EP 0 282 839 B1, employ individual material sources, where material flows have to be controlled individually by a complex control. Furthermore, since the material components do not originate from a single point source and react sensitively on local physical deposition parameters like substrate temperature or gas pressure, deviations of the film composition on a large area are inevitable.

The ideal coating technique would use a point source from which material is emerging with the correct composition at high mass flow, spreading homogenously even over long distances, and depositing on a large area. This ideal is realized in good approximation by electron beam evaporation, where a high-energy electron beam is extremely heating and evaporating the target material. For this reason, this method is used for many technical coating processes for simple compounds or elements, like e.g. aluminum for reflectors and wrapping foil, or simple oxides for optical surface coatings. However, it is problematic to evaporate mixtures of material where the individual components are strongly differing in vapor pressure, or compounds that are chemically destroyed upon electron beam irradiation (cracking) or fractionate.

JP 0 12 64 114 A describes such a method for depositing high temperature superconductor films. However, the results achieved therewith are poor. If such mixtures or compounds are evaporated from a single crucible, they fractionate and due to the continuously changing local thermal conditions the composition of the evaporating material changes with time. This problem can be faced by a rapid deflection of the electron beam into several, independent crucibles and the respective dwell times. However, this again means accepting the disadvantages of

multiple, locally separated sources, i.e. gradients in the composition across larger areas.

For this reason JP 6 11 95 968 A describes an alternative method for the
5 fabrication of alloy coatings, where the alloying components are filled in variable
- sized sector - shaped pockets of a rotating evaporation source. In this way, by
fast rotation under a continuous electron beam on temporal average the desired
composition can be evaporated from one spot. The problem of this arrangement,
however, is that the capacity of the crucibles is limited and a continuous refilling
10 is ruled out due to the rotation. The method is therefore not appropriate for
continuous long - term coating, which requires a large volume of material. The
same applies for similar devices with revolving electron beam evaporator sources
as described in JP 20 02 097 566 A, which enable selective evaporation of
different materials, or the arrangement disclosed in JP 02 294 479 A, which
15 prevents the electron beam from "digging in" and which guarantees an
unchanging fresh surface of the evaporation material.

For continuous production the material supply plays a crucial role. For static
evaporator crucibles such refilling devices are known e.g. from JP 61 003 880 A.
20 Evaporation from a static crucible or gradual evaporation even from a crucible in
motion leads to fractioning of complex compounds, like e.g. oxidic high
temperature superconductors, and to problems with the chemical composition of
the coating. The reason is that within the evaporator crucible no equilibrium is
reached because the local thermal and chemical conditions are continuously
25 changing.

A possible way out is the so called „flash evaporation“ of individual material
grains. Thereby small quantities (grains) of evaporation material are evaporated
sequentially and quantitatively, i.e. essentially without residues. Thereby the
30 vapor on temporal average over several grains is forced to exhibit the same
composition as the evaporation material. Generally speaking, the almost

instantaneous evaporation of a portion of material is of minor importance for quantitative evaporation compared to the establishment of an equilibrium within the evaporation zone between evaporation by the electron beam and the continuous material supply.

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A first attempt for this kind of evaporation is described by Davis et al. in J. Appl. Phys. 66, (1989) 4903. The authors tried to fabricate oxide superconductor films by evaporating a thin line (trace) of powder of the respective evaporation material from front to back by an electron beam. At the hot front, individual powder grains
10 should continuously evaporate in fractions of a second. The results of these experiments, however, were not satisfactory. Since the initial powder material exhibits a large internal surface and is partially hygroscopic, the grains absorb a lot of water. Upon strong heating the water evaporates instantaneously leading to explosions of the powder grains, which hurl them out of the evaporation zone
15 instead of transferring them into the gas phase. For this reason a two – step process was used. In a first step, applying the electron beam at much lower power level, the powder was degassed and melted into small droplets. In the second step, it was tried to transfer these droplets into the gas phase by flash evaporation.

20 Davis et al. used the flash evaporation in combination with another processing step for fabricating the high temperature superconductor, by first evaporating the material in the mentioned way in high vacuum and then re-crystallizing the deposited amorphous material in an oxygen ambient, using either a heating device within the evaporation chamber at reduced oxygen pressure (“in situ”), or a
25 furnace with oxygen at atmospheric pressure (“ex situ”).

Because of the above explained processing route of Davis et al. for flash evaporation it is immediately clear that this method is not appropriate for larger quantities of material or for continuous operation. In addition, the evaporation
30 zone is shifting continuously along the trace. Furthermore, it turned out that the droplets with a mass of around 0.1 g were already too big to be transferred into

the gas phase instantaneously. Concentration depth profiles of the composition of a layer which was formed by evaporating a single droplet – in this case $\text{YBa}_2\text{Cu}_3\text{O}_7$ – exhibit distinct fractioning with strong Ba –enrichment towards the film surface. For this reason, the films have to be thermally annealed and even
5 after that exhibit poor quality.

The problem underlying the present invention is to establish a device and a method to deposit a coating material onto a substrate, that can be operated economically at high rates on the one hand, and results in high quality films on the
10 other hand, and in this way overcomes the mentioned disadvantages of the state of the art.

3. Summary of the invention

According to a first aspect the present invention relates to a device for depositing
15 a high temperature superconductor onto a substrate in vacuum comprising a refilling device for containing a stock of high temperature superconductor material, an evaporation device, that evaporates the high temperature superconductor material within an evaporation zone by means of an energy transferring medium beam, and a conveyor that transports the high temperature
20 superconductor material continuously from the refilling device to the evaporation zone in such a way that the high temperature superconductor material delivered into the evaporation zone is evaporated essentially without residues.

With the device according to the invention, equilibrium is reached within the
25 evaporation zone between the continuous evaporation of material by the energy transferring medium and the continuous material supply by the conveyor. Since the evaporation essentially without residues at a constant rate (adjustable by the material supply) occurs essentially in equilibrium and from an essentially stationary point source, a sophisticated rate control is not necessary and the
30 composition of the deposited film is more homogenous across the entire deposition area than with already known deposition techniques. Further, in the

device according to the invention the substrate can be placed very close to the evaporation zone and can cover a large angle in space to increase the evaporation material yield. This is a big advantage over arrangements with several sources (co-evaporation, MBE), which have to keep a certain minimum distance to limit
5 deviations of the composition.

Preferably the beam of the evaporation device is scanned at least in one direction across the evaporation zone, so that the high temperature superconductor material transported by the conveyor into the evaporation zone is preferably first preheated
10 and then evaporated.

In a first preferred embodiment the evaporation device comprises an electron beam evaporator which can be preferably modulated. However, also arrangements for generating other high energy particle beams (e.g. ion beam bombardment) or
15 using Lasers are possible. At present, electron beams are preferred because they are comparatively cheap and can be easily modulated.

Preferably the high temperature superconductor material is delivered in form of a line into the evaporation zone, where the line width is preferably between 3 and
20 30 mm. The high temperature superconductor material is preferably delivered into the evaporation zone as a granulate with a grain size of 0.05 – 0.5 mm, preferably 0.1 - 0.5 mm and most preferably 0.1 – 0.2 mm.

Granular bulk goods are especially easy for refilling. The given parameters ensure
25 that the heat capacity of the individual grains of the high temperature superconductor material is not too large so that they can be evaporated sufficiently fast. A similar argument holds even if the grains are not individually „flash evaporated“, but are evaporated along a somehow longer stretch x, i.e. over a longer period in time. In any case, the fine granularity is important for sufficient
30 statistics, since the material within an individual grain can thoroughly fractionate.

The conveyor comprises preferably of a revolving turntable, and / or a rotating cylinder, and / or a vibration conveyor, and /or a conveyor belt, and /or a screw conveyor or slide. These embodiments, which are only named exemplarily, allow high rotation- and conveying speed and - with a respective power adjustment of the evaporating device - result in a very high deposition rate in the continuous operation mode. The refilling device is preferably realized by a funnel.

The conveyor is preferably cooled, to avoid destruction by the electron beam. The refilling device, however, is preferably heated and contains preferably a separate pumping device. In a particularly preferred embodiment the refilling device is realized by a funnel which can be heated in its lower section and the separate pumping device is a suction pipe, which protrudes into the lower section of the funnel. The preferred granular high temperature superconductor material, especially if it is hygroscopic material, can absorb water, which leads to explosion of the grains under electron bombardment and thereby to the loss of the material from the evaporation zone. The illustrated preferred characteristics of the device prevent this and ensure further that the chamber vacuum is not affected. Alternatively, the granulate can be pre - treated and degassed thermally and can be attached to the conveyor in a sealed cartridge.

According to another preferred embodiment the high temperature superconductor material comprises of a mixture of different compounds, so that during evaporation on temporal average the desired composition of the high temperature superconductor material is deposited to avoid statistic fluctuations of the film composition. Further, thereby the average composition of the high temperature superconductor material to be evaporated can be varied flexibly, e.g. to compensate for an influence of different sticking coefficients onto the substrate on the stoichiometry. The mixing device can be placed inside or outside the vacuum, or the material is pre - mixed from different components.

Further the device contains preferably means that enable a gas supply close to the substrate, as described in DE 19 680 845 C1. Thereby it is possible to compensate for the loss of gaseous components of the evaporation material during evaporation.

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According to a further aspect, the present invention relates to a method to evaporate a high temperature superconductor coating onto a substrate in vacuum, comprising the steps of continuous delivery of granular high temperature superconductor material into an evaporation zone and the operation of a beam of
10 an energy transferring medium, so that the delivered granulate is evaporated in the evaporation zone essentially without residues.

Preferably the granulate is supplied into the evaporation zone in the shape of a line, where the beam of the energy transferring medium is guided over one end of
15 the line, so that the line is scanned essentially across its entire width and over a small section in the direction of the conveying motion.

Further developments of the device and the method according to the invention are the subject of further depending patent claims.

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4. Short description of the drawings

In the following the preferred embodiments of the invention are explained in detail with reference to the following drawings, which depict:

25 Fig. 1: Schematic sketch of a preferred embodiment of the device according to the invention viewed from top;

Fig. 2: Schematic cross section of a preferred embodiment of the device according to the invention with a funnel as refilling device;

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Fig. 3: Schematic cross section of a preferred embodiment of the device

according to the invention with electron beam evaporator, material refilling, and substrate holder;

- 5 Fig. 4: Schematic cross section of a preferred embodiment of the device according to the invention with electron beam evaporator, substrate holder, and material storage container which can be heated and pumped;
- 10 Fig. 5: Detailed drawing of a heatable refilling funnel with suction pipe;
- Fig. 6a: Evaporation zone of the device (broken line) at the end of the material trace. The direction of transport is marked by the arrow.
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- 15 Fig. 6b: Power profile of the electron beam along the transport direction x according to a first embodiment;
- Fig. 6c: Average thickness, respectively quantity D of the material trace at the entrance into the evaporation zone;
- 20 Fig. 7a: Power profile of the electron beam in the transport direction according to another preferred embodiment;
- Fig. 7b: Thickness profile $D(x)$ of the evaporation material in the evaporation zone if the power profile of Fig. 7a is employed;
- 25 Fig. 7c: Preferred focusing of the electron beam for the power profile of Fig. 7a;
- 30 Fig. 8a,b: Schematic drawing of the inclination of the conveyor (Fig. 8a) and the substrate (Fig. 8b) for compensation of the inclined directional pattern of the evaporating material; and

Fig. 9: Combination of two evaporation devices for a symmetric directional pattern of the evaporating material.

5 **5. Detailed description of the invention**

In the preferred embodiment of a device according to the invention as depicted in Fig. 1, a several millimeter to several centimeter wide trace 4 of fine - granular material 13 is placed onto a conveyor realized in form of a cooled turntable 3 made of material with good heat conductivity, preferably copper, and delivered
10 into an electron beam evaporator 1. For this purpose, the material 13 is applied in well - measured doses from a big reservoir by a continuously operating refilling device 5 onto the conveyor 3 as a line or trace 4 which is several millimeters to several centimeters wide.

15 The conveyor 3 extracts this trace 4 from the refilling device 5 and delivers it into the hot evaporation zone of an electron beam 2. Thereby the trace 4 is then evaporated continuously and essentially without residues. Therefore the beam 2 can be scanned across the line width or is sufficiently wide. The evaporation rate can be controlled by the rotation – or conveying speed of the conveyor 3 and the
20 cross section of the line 4. In particular, very high evaporation rates can be realized in long term operation by respectively high conveying speed and power of the electron beam 2.

Quantitative evaporation, i.e. essentially without leaving residues, can be achieved
25 if within a spatially very narrow evaporation zone of a few millimeter length an equilibrium is established between the continuous evaporation of material by the electron beam 2 and the material supply. Therefore, as depicted in Fig 6a the electron beam 2 can be scanned across an area (broken line) covering the tip of the incoming material trace 4 completely, and its intensity can be modulated. Modern
30 electron beam evaporators offer these options.

According to a first embodiment the power of the electron beam 2 is modulated in such a way (cf. e.g.. Fig. 6b) , that the new incoming material is first pre - heated at lower power level and upon advancing into the hot evaporation zone is first melted and then essentially completely evaporated. At the other end of the
5 evaporation zone the power P of the electron beam 2 should be such high that essentially no residues are left on top of the conveying device 3.

Fig. 6c shows the spatial variation of the thickness $D(x)$ of the material trace 4, respectively the average material quantity of the trace 4. Even if in this
10 arrangement the various components of the evaporation material originate from different sections of the hot evaporation zone, after a short initial phase upon continuous operation an equilibrium is established, so that on average always the composition given by the evaporation material is evaporated. Since the area
covered by the electron beam 2 extends only a few millimeters in the x-direction
15 of the incoming material trace 4, the ideal concept of a point source is realized in good approximation.

To achieve high evaporation rates it has turned out as advantageous to apply the material trace 4 up to several centimeters wide (y-direction) and very thin. This
20 avoids the formation of excessively large droplets when the material 4 melts in the entrance region of the hot evaporation zone, so that statistic variations are kept small.

With the device and the method according to the embodiments of the present
25 invention oxide high temperature superconductor films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO), $\text{DyBa}_2\text{Cu}_3\text{O}_7$ (DyBCO), and $\text{NdBa}_2\text{Cu}_3\text{O}_7$ (NdBCO) have been fabricated. However, the device and method can also be used to fabricate the other coatings named in the introduction. In general, as high temperature superconductor preferably $\text{RBa}_2\text{Cu}_3\text{O}_7$ (R = yttrium, or an element with atomic number 57 to 71,
30 or a mixture of these elements) is possible. Granular material with a slight copper excess and 0.1 mm grain size has been applied by a funnel 5 in shape of a 3 – 30

mm wide, and 0.1 – 1 mm thick trace 4 onto a copper turntable, and was extracted from the bottom of the funnel 5 by continuous rotation, and delivered to the electron beam 2. Oxygen was directly supplied at the about 680°C hot substrate 7, which could be moved to prevent thickness variations, so that an epitaxial
5 superconductor film was deposited at a deposition rate of 0.4 nm/s. However, by adjusting the rotation speed of the turntable 3 and the power of the electron beam evaporator 2 evaporation rates in excess of 2 nm/s could be realized without problems. The superconductor films fabricated on MgO single crystals exhibit transition temperatures of 87 K and critical current densities in excess of 2
10 MA/cm², which is rated as excellent quality for applications.

The granulate to be evaporated should preferably have a grain size between 50 µm and 500 µm. If the grains are smaller or bigger, it is possible, especially at higher
evaporation rates, that they are dispersed by the electron beam 2 and are therefore
15 not evaporated properly. These eruptions can constitute a loss of material and deviations from the stoichiometry. If this occurs actually, however, depends on the setup of the entire system.

The stoichiometry is particularly critical for high temperature superconductors.
20 Preferably it has to be maintained within 1 – 2 % accuracy to reproduce particularly good superconducting properties. This is a much more stringent requirement than necessary for example for fabrication of glasses or alloys. The repetition frequency for the scan of the electron beam 2 should be preferably as high as possible, but preferably at least 50 Hz, to minimize the dispersion of the
25 evaporation material 4 by eruptions at higher evaporation rate.

To control the process a continuous measurement of the evaporation rate of the high temperature superconductor is preferred. For a long term deposition process quartz rate monitors are only poorly applicable, since they are saturated rapidly.
30 Instead, the rate can be preferably measured by atomic absorption spectroscopy (AAS) (not shown). For that, however, at least one component of the evaporating

material 4 must not be present in molecular form as an oxide, but in atomic form as an element.

It has turned out that upon electron evaporation of high temperature
5 superconductors the Cu - component is always present in atomic form. Therefore,
it is advantageous to determine the total evaporation rate of the superconductor by
using the AAS of the Cu - line. At the aimed high evaporation rates and large
diameters of the vapor beam for large area deposition, however, there may arise
the problem, that the absorption line is saturated. This can be preferably solved by
10 a partial shading of the vapor at the location of the measurement, so that the
absorption preferably occurs only in a multitude of well - defined sections of the
light beam. The positions of the sections can be preferably chosen in such a way
that the respective Doppler shifts of the Cu - absorption line all together cover the
whole spectral width of the light beam. The lengths of the sections are preferably
15 chosen in such a way that the absorption at the desired evaporation rate is
approximately 30%.

Preferably, in combination with the actual high temperature superconductor layer
also further auxiliary layers of different oxide materials are deposited as a base or
20 cap layer. They serve as diffusion barriers, for establishing texture, as seed layer,
or as protection against environmental influence etc. For technical and economic
reasons it is preferred to deposit them onto the substrate 7 sequentially with the
actual superconductor layer in situ, i.e. without breaking the vacuum. For this
reason it is advantageous if it is possible to evaporate different materials
25 sequentially with the same device, e.g. by placing several storage containers 5,
which can each be closed at their bottom outlet, next to each other on top of the
conveyor 3.

For evaporation of a certain material one of the storage containers 5 is opened and
30 the scanning area of the electron beam 2 is adjusted to the respective material
trace 4. The closure at the outlet of the storage container 5 can be e.g. realized by

a plug (not shown), located inside the storage container 5. For fine –grain material the plug just has to block the outlet and does not have to seal it tightly. Hence, it can be lifted (outlet open) or lowered (outlet closed) by a simple mechanism. For lowering, the residual material underneath the plug has to be preferably removed
5 from the outlet by operating of the conveyor 3, before the evaporation of the new material is started. If space is restricted, it may be advantageous not to place the various storage containers permanently on top of the conveyor 3, but to use a mechanism to position only a partial number of storage containers, preferably only a single storage container 5 on top of the conveyor 3. The mechanism can be
10 for example, a revolver, a magazine, or a single lowering device (not shown) for each container.

For further description of variations of the device and the method according to the invention, the currently particularly preferred examples 1 – 10 are explained in
15 more detail in the following:

Example 1:

Granular evaporation material 13 is conducted by a trapezoid funnel 5 onto a rotating, water – cooled copper turntable 3 of an electron beam evaporator 1. Due
20 to the rotation of the turntable 3 a fine trace of material 4 is extracted at the bottom of the funnel 5 and delivered to the electron beam 2 on the opposite side. The power and focus of the electron beam 2 is adjusted in such a way, that upon entering the hot evaporation zone the arriving grains of the evaporation material evaporate rapidly and essentially without residues, i.e. they evaporate
25 quantitatively. The vapor spreads unimpeded within the high vacuum chamber 6 and condenses onto a substrate 7 which can be heated if necessary (cf. Substrate heater 8 in Fig. 3). If required, a reactive gas can also be introduced into the chamber 6 or supplied directly at the substrate 7 by an appropriate device 9, 10.

30 In contrast to the mentioned state of the art of Davis et al. the flash evaporation is used as a one – step technique for fabricating high temperature superconductors.

Therefore, the oxygen necessary for oxidation and crystal formation is supplied directly during the material deposition, using the device 9, 10 according to Fig. 3 and by increasing the substrate temperature by a heater 8.

5 Additionally, the flash evaporation of high temperature superconductors can be used in combination with a moving substrate 7, for example by rotating the substrate 7 in figures 3 and 4 around a vertical axis (not shown). This has the advantage of a more homogeneous stoichiometry on a large area, which is particularly critical for high temperature superconductors. Beyond that, the
10 motion of the substrate is advantageous for depositing on a large number of substrates (e.g. wafer deposition in a series production), or very large substrates (e.g. substrate plates for fault current limiters), or very long tape ("coated conductors"), which are continuously transported through the evaporation zone without interrupting the evaporation process.

15

Example 2:

The setup corresponds to that described in example 1. The granulate 13, however, originates from a closed storage container 5 which can be heated by heater elements 11 and which can be pumped at through a pumping neck to remove
20 released residual gas. With such a setup evaporation rates of 5 nm/s have been achieved. For this, a preferred grain size of 100 – 200 μm has been used and the preferred scanning repetition frequency was 90 Hz. The stoichiometry deviation on an area of 20 cm \times 20 cm was merely 1%.

Example 3:

25 The setup corresponds to that described in example 1. The granulate 13, however, is supplied through a funnel 5, which is heated only in its bottom outlet section by heater elements 11. The thereby released water vapor is pumped away directly at its origin by a suction pipe 12, preferably with a sieve in front of the inlet (not
30 shown).

Example 4:

Granular evaporation material 13 is conducted by a conveyor belt, a screw conveyor or a similar conveyor like a slide (not shown) onto a rotating, water – cooled copper turntable 3 of an electron beam evaporator. Due to the rotation of the turntable 3 a fine trace of material 4 is delivered to the electron beam 2 on the opposite side. The power and focus of the electron beam 2 is adjusted in such a way, that upon entering the hot evaporation zone the arriving grains of the evaporation material 13 evaporate rapidly and essentially without residues, i.e. they evaporate quantitatively. The vapor spreads unimpeded within the vacuum chamber 6 and condenses onto a substrate 7 which can be heated by a substrate heater 8 if necessary. If required, a reactive gas can also be introduced into the chamber or supplied directly at the substrate 7 by an appropriate device 9, 10.

Example 5:

Granular evaporation material 13 is applied by a refilling device , e.g. a trapezoid funnel 5, onto a rotating, water – cooled drum (not shown) and delivered as a fine line to the electron beam 2 of an electron beam evaporator. The power and focus of the electron beam 2 is adjusted in such a way, that upon entering the hot evaporation zone the arriving grains of the evaporation material evaporate rapidly and essentially without residues, i.e. they evaporate quantitatively. The vapor spreads unimpeded within the high vacuum chamber 6 and condenses onto a substrate 7 which can be heated by a substrate heater 8 if necessary. If required, a reactive gas can also be introduced into the chamber or supplied directly at the substrate 7 by an appropriate device 9, 10.

Example 6:

Granular evaporation material 13 is applied by a refilling device , e.g. a trapezoid funnel 5, onto a water – cooled vibration conveyer and delivered as a fine line to the electron beam 2 of an electron beam evaporator 1. The power and focus of the electron beam 2 is adjusted in such a way, that upon entering the hot evaporation zone the arriving grains of the evaporation material evaporate rapidly and

essentially without residues, i.e. they evaporate quantitatively. The vapor spreads unimpeded within the high vacuum chamber 6 and condenses onto a substrate 7 which can be heated by a substrate heater 8 if necessary. If required, a reactive gas can also be introduced into the chamber 6 or supplied directly at the substrate 7 by an appropriate device 9, 10.

Example 7:

Granular evaporation material 13 is applied by a refilling device , e.g. a trapezoid funnel 5, onto a cooled conveyer belt and delivered as a fine line to the electron beam 2 of an electron beam evaporator. The power and focus of the electron beam is adjusted in such a way, that upon entering the hot evaporation zone the arriving grains of the evaporation material evaporate rapidly and essentially without residues, i.e. they evaporate quantitatively. The vapor spreads unimpeded within the high vacuum chamber 6 and condenses onto a substrate 7 which can be heated by a substrate heater 8 if necessary. If required, a reactive gas can also be introduced into the chamber 6 or supplied directly at the substrate 7 by an appropriate device 9, 10.

Example 8:

Material feeding and transport correspond to one of the previous examples 1 – 7. The material trace 4 can have a width of several centimeter. The electron beam 2 is scanned over an area, which covers the width of the arriving material trace 4 completely, e.g. a rectangular area as shown in Fig.6a. Thereby the power P of the electron beam 2 is modulated in such a way, that with proceeding position the arriving material is first pre - heated, melted, and then completely evaporated. An appropriate power profile is shown for example in Fig. 6b. The shape of the profile (e.g. linear, exponential, sinusoidal, etc.) can be chosen appropriately. In this context it is mainly important that the peak power is set sufficiently high, so that all the material evaporates essentially without residues. In this case, for example a thickness profile as shown in Fig. 6c may be established.

Example 9:

According to a further embodiment a preferable 2 – stage profile is used with essentially two power levels for the electron beam 2 as shown in Fig. 7a. Thereby the power level P_1 is preferably chosen in such a way that the material is annealed
5 but the temperature is not sufficient to evaporate components of the high temperature superconductor, particularly Cu. The power level P_2 is preferably chosen such that the high temperature superconductor is evaporated quantitatively. The transition width Δx between the two zones is preferably as narrow as possible, so that the material evaporates instantaneously quantitatively.
10 Then, a linear slope of the thickness profile $D(x)$ according to Fig. 7b is established.

If the transition width Δx between the two power zones is not sufficiently narrow, there is a danger, that the upper edge of the slope (i.e. the boundary between the
15 two power zones) is rounded and particularly the copper component of the granulate evaporates with a false directional pattern. To achieve a narrow transition the electron beam has to be preferably focused in such a way, that while scanning it reaches the smallest possible width, when it is located at the upper edge of the slope. This is depicted schematically in Fig. 7c.

20 The inclination angle α of the slope in Fig. 7b is determined by the conveying velocity of the evaporation material v_F and the evaporation speed of the material trace dD/dt according to $\tan \alpha = (dD/dt)/v_F$. Thereby the angle α can be adjusted for every evaporation speed by the conveying velocity.

25 Since the evaporation material evaporates preferably from the slope, the directional pattern of the evaporating material is inclined by the angle α against the normal of the conveying device (cf. Fig.7b). In most cases the inclination is disadvantageous for the deposition. Therefore, α should preferably not be bigger
30 than 20° . On the other hand, if the angle α becomes too flat, at a given initial

thickness D_0 of the material trace the length L of the evaporation zone increases according to $L = D_0 / \tan \alpha$. Preferably, L should not be longer than 10 mm, that the material evaporates sufficiently point – like and no noticeable gradients in the stoichiometry result on the substrate. Hence, at a typical thickness $D_0 = 1$ mm
5 preferably α should not be smaller than 6° .

The inclination of the directional pattern of the evaporating material at the angle α can be compensated by inclining the entire conveyor 3 including the conveyor trace 4 by essentially the same angle in the opposite direction. This is shown
10 schematically in Fig. 8a. However, if the inclination angle is too big, the transport of the evaporation material can be impeded when the trace 4 on top of the conveying device 3 begins slipping. This problem is avoided by another option to compensate the angle α by inclining the substrate 7 correspondingly. This is
shown schematically in Fig. 8b.

15

Example 10:

To arrive at a symmetric directional pattern of the evaporating material despite the inclination at an angle α , according to another embodiment two or more evaporation devices can be employed, too. E.g. two evaporation devices can be
20 preferably placed next to each other, so that the evaporation zones are facing each other. This is shown in Fig. 9. The evaporation rates of both devices should preferably coincide in this case.

Legend of reference numbers:

	1	Electron gun
	2	Electron beam
5	3	Turntable (rotating)
	4	Material trace (line)
	5	Refilling device (funnel, storage container)
	6	Vacuum chamber
	7	Substrate
10	8	Substrate heater
	9	Reactive gas supply
	10	Gas inlet
	11	Heating element
	12	Suction pipe
15	13	Granulate

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